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Division of Multidisciplinary Chemistry
– Molecular Rheology –

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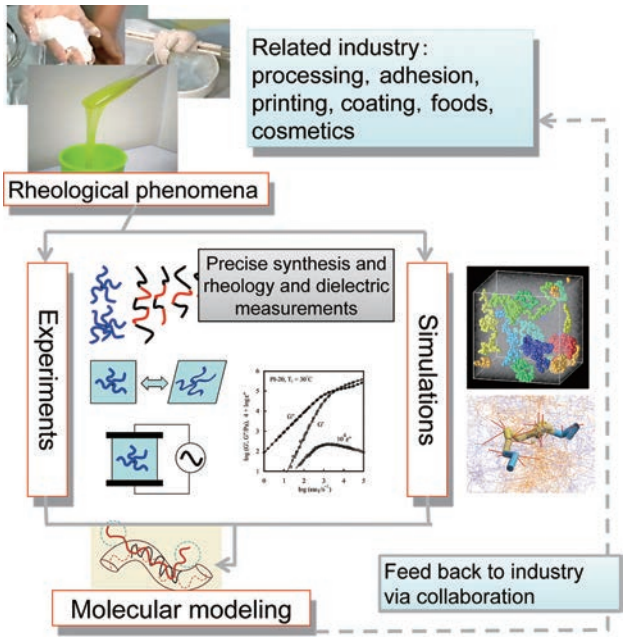
Scope of Research

Research focus is placed on the molecular origin of rheological properties of various materials. Depending on time and temperature, homogeneous polymeric materials exhibit typical features of glass, rubber, and viscous fluid while heterogeneous polymeric systems exhibit plasticity in addition to these features. For basic understanding of these features, the molecular motion and structures at various scales are studied for polymeric systems in deformed state. Rheological measurements are performed with various rheometers. Auto-correlation of the molecular orientation is also investigated with dynamic dielectric spectroscopy. Analysis of rheological and dielectric behavior elucidates new aspect of softmatter physics.



KEYWORDS

Rheology Dielectric Spectroscopy Softmatter

Selected Publications

Watanabe, H.; Matsumiya, Y.; Kwon, Y., Dynamics of Rouse Chains undergoing Head-to-Head Association and Dissociation: Difference between Dielectric and Viscoelastic Relaxation, *J. Rheol.*, **61,** 1151-1170 (2017).

Kwon, O. M.; Watanabe, H.; Ahn, K. H.; Lee, S. J., Growths of Mechanical Elasticity and Electrical Conductance of Graphene Nanoplatelets/Poly(lactic acid) Composites Under Strong Electric Field: Correlation with Time Evolution of Higher Order Structure of Graphene Nanoplatelets, *Rheol. Acta*, **56,** 871-885 (2017).

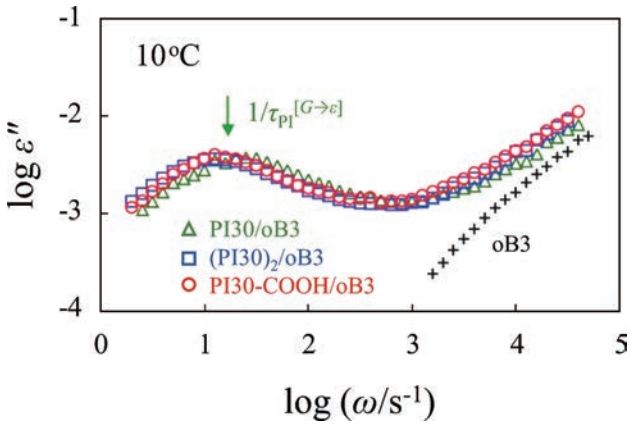
Watanabe, H.; Matsumiya, Y., Revisit the Elongational Viscosity of FENE Dumbbell Model, *J. Soc. Rheol. Jpn.*, **45,** 185-190 (2017).

Doi, Y.; Matsumoto, A.; Inoue, T.; Iwamoto, T.; Takano, A.; Matsushita, Y.; Takahashi, Y.; Watanabe, H., Re-Examination of Terminal Relaxation Behavior of High-Molecular-Weight Ring Polystyrene Melts, *Rheol. Acta*, **56,** 567-581 (2017).

Kwon, O. M.; Watanabe, H.; Ahn, K. H.; Lee, S. J., Interplay between Structure and Property of Graphene Nanoplatelet Networks Formed by an Electric Field in a Poly(lactic acid) Matrix, *J. Rheol.*, **61,** 291-303 (2017).

Dynamics of Rouse Chains undergoing Head-to-Head Association and Dissociation: Difference between Dielectric and Viscoelastic Relaxation

For monofunctionally head-associative Rouse chains having type-A dipoles, the Rouse equation of motion was combined with the association/dissociation kinetics to calculate the dielectric relaxation function, $\Phi_j(t)$ with $j = 1$ and 2 for unimer and dimer. $\Phi_1(t)$ reflects the orientation of the end-to-end vector of the unimer, whereas $\Phi_2(t)$ detects the orientation of two end-to-center vectors of the dimer (having symmetrical dipole inversion), both being in the direction of the applied electric field. The calculation was made by mapping the conformation of dissociating dimer onto the created unimer and vice versa with the aid of the Rouse eigenmode expansion of the bond vector of segments (Gaussian subchains). It turned out that $\Phi_j(t)$ is not influenced by the association/dissociation reaction. This result makes a striking contrast to the behavior of the viscoelastic relaxation function $g_j(t)$: $g_j(t)$ is strongly affected by the motional coupling between the unimer and dimer due to the reaction. This difference emerged because the dielectric $\Phi_j(t)$ corresponds to the vectorial first-moment average of the segmental bond vector at time t, $\mathbf{u}(n,t)$ with n being the segment index, whereas the viscoelastic $g_j(t)$ corresponds to the tensorial second-moment average. Because of this difference in the averaging moment, $\Phi_j(t)$ is subjected to cancelation in the conformational mapping but $g_j(t)$ is not, so that the reaction effect emerges only for $g_j(t)$. The experimental data of head-carboxylated high-*cis* polyisoprene chains (having the type-A dipoles) confirms this difference; see Figure.



Revisit the Elongational Viscosity of FENE Dumbbell Model

The dumbbell model with a finite extensibility was developed almost a half century ago as a model for those chains under strong flow. This model exhibits the finite extensible nonlinear elasticity (FENE) effect under strong flow to provide the elongational viscosity η_E with the strain-hardening feature but without any divergence. This study focuses on the effective relaxation time τ_{eff}^F of the FENE dumbbell under steady elongational flow by taking into account stiffening of the FENE dumbbell. It turned out that the stiffening of the FENE dumbbell leads to a decrease of τ_{eff}^F in proportion to $\dot{\varepsilon}^{-1}$ at $\dot{\varepsilon} > 1/2\tau_{eq}^H$, where $\dot{\varepsilon}$ is the elongational strain rate. This decrease of τ_{eff} allows the effective Weissenberg number of the FENE dumbbell under flow, $Wi_{eff}^F = \dot{\varepsilon}\tau_{eff}^F$, to stay below a critical value of ~1/2 even for $\dot{\varepsilon}\to\infty$. This limited increase of Wi_{eff}^F allows the FENE dumbbell to change its conformation just slightly even for a large increase of $\dot{\varepsilon}$ from $1/2\tau_{eq}^H$ to any higher value, which naturally leads to the lack of divergence of η_E.